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Toward the Biaxial Nematic Phase of Low Molar Mass Thermotropic Mesogens: Substantial Molecular Biaxiality in Covalently Linked Rod−Disk Dimers

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Since the prediction of the biaxial nematic phase by Freiser,[1] there has been considerable interest in the demonstration of this phase as a physical reality, and extensive debate in the literature concerning the validity, or otherwise, of putative examples.[2] In the uniaxial nematic phase (N_u) of liquid crystals, there is no positional order, and the unique axes of the molecules are oriented about a director, **n**. In the biaxial nematic phase (N_b) there is, additionally, a correlation of the molecules in a direction perpendicular to **n**; therefore, whereas in the N_u phase the physical properties in the plane perpendicular to **n** are angle-independent, in the N_b phase this is not the case. A simple schematic representation of the N_b phase composed of lozenge-shaped molecules is shown as Figure 1.

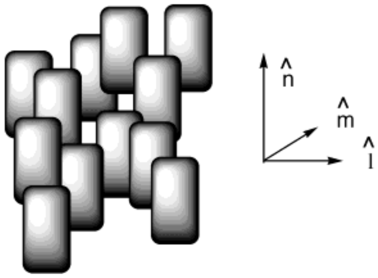

Figure 1. Representation of a biaxial nematic phase

In 1980, Yu and Saupe[3] published what is accepted as a genuine example of the biaxial nematic phase formed by a ternary lyotropic system, although some doubts about even this system have been expressed.[4] Then, Hessel and Finkelman[5] published a paper describing a side-chain liquid crystal polymer in which the mesogenic group was attached laterally. This material was also claimed to have a N_b phase, and this claim has not, to our knowledge, been disputed. However, in low-molar-mass thermotropic liquid crystals, unequivocal proof of a N_b phase remains to be given, despite several claims to the contrary. One of the principal issues centers around how a biaxial nematic phase may be identified; this is reviewed by Galerne.[6]

In considering a molecular design for a putative biaxial material which can display three, orthogonal directors, several options are apparent. One is to employ a shape biaxiality,[7] another is to design in molecular biaxiality (i.e. the extent to which the molecule and/or its interactions deviate from those associated with cylindrical symmetry), while another is somehow to mix rods and disks. Using this last approach, theoretical work by Sharma et al.[8] and by Vanakaras et al.[9] has shown that rod−disk mixtures can lead to N_b phases if the rod and the disk are attracted more to one another than to each other. This attractive interaction is required otherwise the mixtures simply separate into two uniaxial nematics.[10]

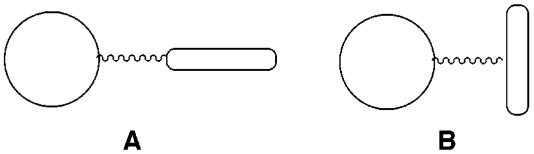

Figure 2. Rodlike moiety attached end-on (A) and side-on (B) to disk.

In the extended Onsager approach adopted by Vanakaras et al., the attractive interactions used in the simulation had a strength of the order of hydrogen bonds, but an alternative strategy, and one which is guaranteed to avoid phase separation, is to link the rod and disk covalently. One such example is known[11] based on a pentayne disk and a cyanobiphenyl moiety which were linked according to Figure 2A, although it showed only a strongly monotropic mesophase. However, with this idea in mind and taking account of the seemingly successful approach adopted by Hessel and Finkelmann, we undertook the design and synthesis of a rod−disk mesogen in which the rod would be attached laterally to the disk according to Figure 2B. Thus, the molecule, shown in Figure 3 (X = H), contains a pentayne disk as described by Janietz et al.[12] joined to the lateral rod described by Hessel and Finkelmann.[5]

Examination by polarized optical microscopy shows that the material possesses a monotropic nematic phase which is very viscous and does not readily crystallize. There is evidence of a schlieren texture, and two-brush defects are clearly seen, although the presence of four-brush defects is less obvious. Chandrasekhar has previously suggested that the observation of only two-brush defects can confirm the presence of a biaxial nematic phase, although this is in doubt, especially with the recent observation of this texture in the biaxial smectic A phase.[13] Evaluation of the thermal characteristics of these transitions by differential scanning calorimetry showed typical values of the molar enthalpy and entropy changes on melting, but the same parameters measured on passing from the nematic to the isotropic phase were very small (Figure 3). Molecular field theory predicts that the biaxial-nematic-to-isotropic phase transition is second order,[14] and therefore the small thermal parameters observed are rather encouraging.

To determine the symmetry of the nematic phase, we undertook some deuterium NMR experiments; thus, we synthesized a material in which the protons of the phenyl groups which are ortho to the alkyne groups were selectively deuterated (Figure 3, X = D). We first tried to obtain a ^{2}H NMR spectrum of the neat

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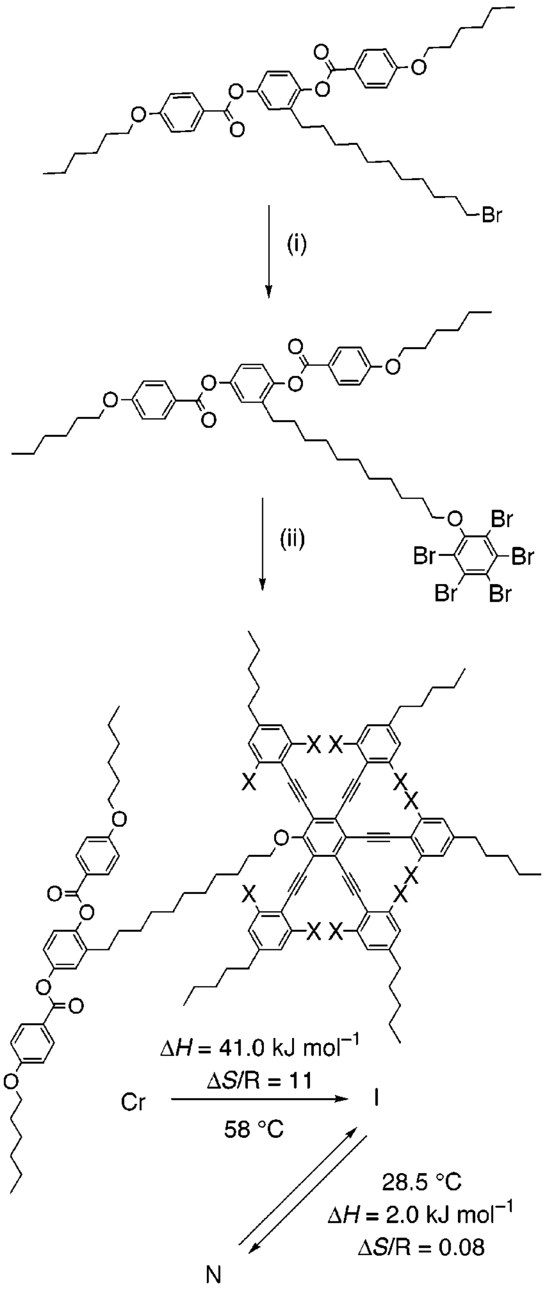

Figure 3. Synthesis and structure of the rod-disk dimer and its thermal behavior. (i) HOC_6Br_5/NaH/DMF; (ii) $C_5H_{11}C_6H_2X_2C{\equiv}CH$/CuI/[$PdCl_2(PPh_3)_2$]/$PPh_3$. Details in the Supporting Information.

material in its nematic phase, but its viscosity is so high that only a single, broad line was observed and not the quadrupolar doublets found for conventional nematics. This would be consistent with the low degree of orientational order expected from the small transitional entropy. Next, we attempted to characterize the degree of molecular biaxiality, as opposed to phase biaxiality, by dissolving the dimer (5 wt %) in the eutectic mixture of cyanobiphenyls known as E7 (from Merck). At this concentration, the dimer will not perturb the symmetry of the N_u phase of E7. From this nematic solution, we obtained a spectrum (Figure 4) showing two quadrupolar splittings of 56 337 Hz and 16 734 Hz at 295 K. The intensity of the smaller quadrupolar splitting is essentially four times that of the larger quadrupolar splitting. These are interpreted as follows.

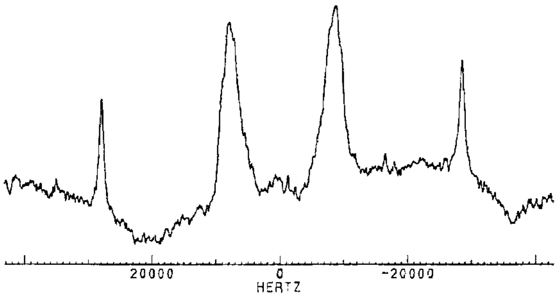

Figure 4. ^{2}H NMR spectrum of the dimer dissolved in E7.

First, we start by recognizing that E7 possesses a positive diamagnetic anisotropy so that the rodlike molecules which constitute the mixture will align parallel to the magnetic field. Second, we make the assumption that the rod part of the dimer will align itself with the director of E7. Thus, we have to address the orientation of the pentayne ring. We begin our analysis by assuming that the average plane of the disk is parallel to the orientation of the rodlike part and, hence, to the rods of E7. We then attribute the smaller splitting of 16 734 Hz to the deuterium nuclei located on disk phenyl groups situated in positions 2-, 3-, 5-, and 6- relative to the central phenyl ring because of its stronger intensity. Similarly, the larger splitting must be associated with the deuterons in the single phenyl ring at the 4-position. The fact that the splittings for the two classes of deuterons have these relative magnitudes is consistent with the pentayne disk being arranged with the 1,4-axis tending to be aligned perpendicular to the director. In other words, the average conformation of the dimer tends to be like that sketched in Figure 2B which will align in a calamitic nematic with the rod parallel to the director, the symmetry axis of the disk orthogonal to it, and the 1,4-axis also orthogonal to the director.

To determine the principal components of the Saupe ordering matrix, **S**, for the disk from the two quadrupolar splittings requires that we know their signs, but these are not available from the NMR spectra. We have assumed, therefore, that the effective shape of the rod−disk dimer is indeed that shown in Figure 2B which will align in the calamitic nematic such that the larger splitting is positive, while the smaller splitting is negative. Now to evaluate the principal components of **S** we need the effective geometry of the pentayne disk and take the rings to be twisted out of the plane of the central phenyl ring by 30°.[15] With these assumptions we find that at 295 K, the average ordering matrix for the disk unit has a major component, $S_{zz} = 0.553$ and a biaxial part, $S_{xx} - S_{yy} = 0.379$. This biaxiality in the ordering matrix is relatively large[16] and indicates that the combination of rod and disk units in a single molecular entity has created a highly biaxial molecule. This approach could well provide an example of a low-molar-mass, thermotropic biaxial nematic.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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